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Influence of Process Parameters on the Reaction Kinetics of the Chromium-Catalyzed Trimerization of Ethylene

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Abstract: In this paper we report the results of an extensive experimental kinetic study carried out on the novel ethylene trimerization catalyst system, comprising the chromium source $[CrCl_3(thf)_3]$ (thf = tetrahydrofuran), a Ph_2P-N(*i*Pr)-P(Ph)-N(*i*Pr)H (PNPNH) ligand (Ph = phenyl, *i*Pr = isopropyl), and triethylaluminum ($AlEt_3$) as activator. It could be shown that the initial activity shows a first-order dependency on the ethylene concentration. Also, a first-order dependency was found for the catalyst concentration. The initial activity follows a typical Arrhenius behavior with an experimentally determined activation energy of 52.6 kJ mol^{-1}. At elevated temperatures (ca. 80 °C), a significant deactivation was observed, which can be tentatively traced back to a ligand rearrangement in the presence of $AlEt_3$. After a fast initial phase, a pronounced 'kink' in the ethylene-uptake curve is observed, followed by a slow, almost linear, further increase of the total ethylene consumption. The catalyst composition, in particular the ligand/chromium and the cocatalyst/chromium molar ratio, has a strong impact on the catalytic performance of the trimerization of ethylene.

Keywords: chromium · homogeneous catalysis · kinetics · N,P ligands · oligomerization

Introduction

The existing technologies for producing linear alpha-olefins (LAOs) are mostly based on ethylene oligomerization routes through an ethylene insertion/β-elimination mechanism resulting in a mathematical product distribution like Schulz–Flory or Poisson.[1] Thus, the conventional full-range producers (e.g., Shell, Chevron Phillips, INEOS, UNITED) have to meet a formidable challenge to match the market demand. The reason is that the size and growth of each market segment strongly depends on the 1-olefin chain length. Through the increasing demand for the high-value comonomer fraction (C6 and C8) in recent years, many industrial and academic research groups focused their interest on selective oligomerization, in particular, the tri- and tetramerization of ethylene.[2] Consequently, the number of patents and scientific publications for intentional routes to 1-hexene and even 1-octene increased drastically in recent years.

The most prominent and one of the earliest highly selective catalysts was developed by Chevron Phillips in the late 1980s,[3] yielding 1-hexene in an overall selectivity greater than 90 %. After various improvements, the Chevron Phillips chromium-based catalyst became the basis of the first commercialized trimerization technology, implemented in a 47 000 t a^{-1} plant in Qatar that went successfully on stream in 2003.[4]

However, to reach the extraordinary selectivity for obtaining 1-hexene, the traditional insertion/β-elimination mechanism has to be overcome. The selectivity towards 1-hexene is explained by a metallacycle mechanism (Scheme 1), which was proposed initially by Manyik et al.[5] and expanded later by Briggs.[6] This widely accepted mechanism could be supported by several studies for ethylene trimerization.[7]

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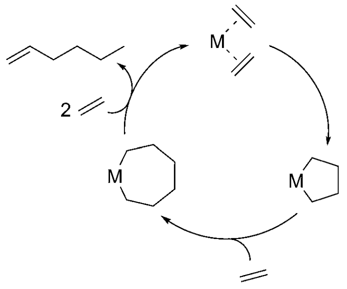


Scheme 1. Metallacycle mechanism for ethylene trimerization proposed by Briggs.[6]

In general, selective oligomerization catalysts are complex systems that consist of a transition metal, a ligand, and mostly of an aluminum alkyl as cocatalyst. Besides the usage of early transition metals (Ti,[8] Zr,[9] V,[10] Ta[7b,11]), in the majority of all cases, homogeneous chromium-based ethylene-trimerization catalysts are used. The most commonly used ligands consist of aromatic or multidentate structures with phosphine, amine, ether, or thioether donors.[2] To elucidate the necessary characteristics of these ligands to catalyze the selective oligomerization, a great number of studies were conducted investigating the influences of different ligand substituents, for example, for Sasol's tri- and tetramerization catalyst system[12] or other trimerization systems.[13]

While the understanding of the catalytically active species for selective tri- and tetramerization increased in recent years, unfortunately only few publications[8a,14–16] deal with kinetic investigations, although they are essential for the understanding of the catalytic mechanism and help to elucidate the complex reaction network. With a good comprehension of the influence of reaction conditions, the process can be designed and even optimized, in particular, with regard to activity, selectivity, and stability. Moreover, kinetic measurements form the basis for the design of a pilot- and, eventually, a technical-scale plant.

Table 1 gives an overview of reported kinetic measurements. Some discrepancies regarding the influence of ethylene concentration are noteworthy. For instance, Manyik et al.,[5] Yang et al.,[17] and Wass et al.[13e] reported an experimental second-order rate dependency on ethylene concentration for three different chromium-based trimerization catalyst systems. These results led to the conclusion that the rate-determining step is the formation of a metallacyclopentane intermediate from two coordinated ethylene molecules.

Contrary to these results, modeling studies carried out by van Rensburg et al.[18] for a "Cr–pyrrolyl" catalyst support a first-order dependency with respect to ethylene concentration. Budzelaar et al.[19] as well as Tobisch and Ziegler[20] theoretically investigated the titanium-catalyzed trimerization mechanism and also identified the metallacycle growth as the rate-determining step, consequently leading to a first-order dependency. In contrast, a DFT study conducted by Raybaud et al.[21] for a titanium-based system proposed that the ring-opening reaction of the seven-membered metallacycle is rate determining. Kuhlmann[15] found in his experimental studies of the "Cr–PNP" system a first-order ethylene dependency for the trimerization reaction and a second-order dependency for the tetramerization. This results in a overall reaction order of 1.71, which is in good agreement with the observed noninteger reaction order of 1.57 by Walsh et al.,[14] suggesting a competition of two different pathways for tri- and tetramerization.

As a result of the different studies and their inconsistencies, one can speculate that the differences in catalytic systems lead to a different kinetic behavior as well. For a better understanding of the metallacycle mechanism, further detailed kinetic investigations are vitally important.

In their extensive report on kinetic measurements for the ethylene tri- and tetramerization system consisting of the precatalyst [Cr(acac)$_3$] (acac = acetylacetonate), Ph$_2$PN(*i*Pr)PPh$_2$ as ligand, and methylaluminoxane (MAO) as activator, Walsh et al.[14] found that the initial reaction rate follows a typical Arrhenius behavior with an apparent activation energy of 64.6 kJ mol^{-1} in the temperature range between 35 and 45 °C. However, above 45 °C the deactivation rate is strongly influenced by temperature, which is consistent with findings by Kuhlmann.[15] Although Sasol's "Cr–PNP" tetramerization system is highly sensitive to elevated temperature, like other trimerization systems,[13] the "Cr–^{MeO}PNP" trimerization catalyst system shows, for example, nearly no deactivation at 110 °C.[13]

In this paper we report the results of an extensive experimental kinetic study carried out on the novel ethylene trimerization catalyst system comprising the chromium source [CrCl$_3$(thf)$_3$] (thf = tetrahydrofuran), a Ph$_2$PN(*i*Pr)P(Ph)N(*i*Pr)H (PNPNH) ligand (Ph = phenyl, *i*Pr = isopropyl), and triethylaluminum (AlEt$_3$) as activator.[22,23] The influence of temperature, residence time, ethylene concentration, catalyst composition, and concentration on the catalytic trimerization reaction

Table 1. Overview of reported experimental kinetic measurements of selective ethylene tri- and tetramerization processes.

Catalyst system[a]	Product	Reaction order [catalyst]	Reaction order [C_2H_4]	E_a [kJ mol^{-1}]	Ref.
Cr(2-EH)$_3$/PIBAO[b]	C6	–	2	"near 0"	[5]
Cr(2-EH)$_3$/2,5-Me$_2$-pyrrole/AlEt$_3$/Cl compound	C6	–	2	–	[17]
[CrCl$_3$(thf)$_3$]/Ar$_2$P(Me)NPAr$_2$/MAO[c]	C6	–	2	–	[13e]
[Cr(acac)$_3$]/Ph$_2$P(*i*Pr)NPPh$_2$/MAO[d]	C6/C8	1	1.57	64.6	[14]
[Cr(acac)$_3$]/Ph$_2$P(THN)NPPh$_2$/MMAO-3A[e]	C6/C8	0.6	1.71	23.1	[15]
TiCl$_3$/Me$_3$SiC$_5$H$_3$Me$_2$C$_6$H$_3$Me$_2$/MAO	C6	1	1	27.7	[8a]

[a] Studies were conducted by using different parameters. [b] Chromium(III)–2-ethylhexanoate/poly(isobutyl aluminum oxide). [c] Ar: *ortho*-methoxyphenyl; MAO = methylaluminoxane. [d] acac = acetylacetonate. [e] THN = 1,2,3,4-tetrahydronaphthyl PNP; MMAO-3A = modified methylaluminoxane, type 3A.

was investigated in detail. The liquid-phase trimerization reaction was performed in a semibatch stirred tank pressure reactor (0.3 L), while isobaric conditions were provided by feeding ethylene on demand. Through recording the ethylene uptake over time, statements about changes in the reaction rate by, for example, catalyst deactivation could be derived easily. Due to the relatively low conversion over time, the reactor showed pseudodifferential behavior, thus providing the required sensitivity for the observation of changes in the reaction rate as a function of process parameter variation. In a separate study, it could be shown that gas-to-liquid phase-transfer limitation could be excluded and the intrinsic kinetics of the ethylene trimerization reaction were observed.

Results and Discussion

In the following, the results of the evaluation of various process parameters and kinetic studies are discussed. For this purpose the ethylene-uptake curve over the oligomerization run time is an integral part of the experimental evaluation. Due to the fact that mass-transfer limitations can be excluded, the consumption of ethylene, monitored over time, can be directly translated into the time characteristics of the catalytic ethylene trimerization. For clarity, the filling process of the reactor's headspace and the rapid mass transfer (gas-phase ethylene to dissolved ethylene) in the beginning of each individual experiment is generally omitted from the illustrations. However, the ethylene-uptake curve includes both the ethylene that is converted to product and the ethylene that is required for saturation of the newly formed product.

Influence of residence time on 1-hexene and by-product formation: To resolve the kinetics of the ethylene trimerization and the formation of the most important by-products, experiments with termination after varying residence times were conducted. As opposed to time-resolved sampling during the experiment, this has the advantage that the reaction is not disturbed by the removal of samples. Furthermore, an entire mass balance, including gas-phase product, can be determined for each timescale.

The measured ethylene-uptake curves of the conducted experiments are consistent with the example shown in Figure 1. It illustrates clearly the complex time characteristics of the ethylene-uptake curve with its steep initial slope, followed by a 'kink' and, finally, a slow, almost linear, further increase.

The kink kinetics observed in the ethylene-uptake curve is also reflected by the concentration–time profile of 1-hexene (Figure 2) and is, therefore, an intrinsic property of the ethylene trimerization reaction. In conjunction with the fact that more than 90 wt % of the product is 1-hexene, conclusions about the kinetics drawn from the ethylene-uptake curve are in good accordance with the kinetics of the 1-hexene formation.

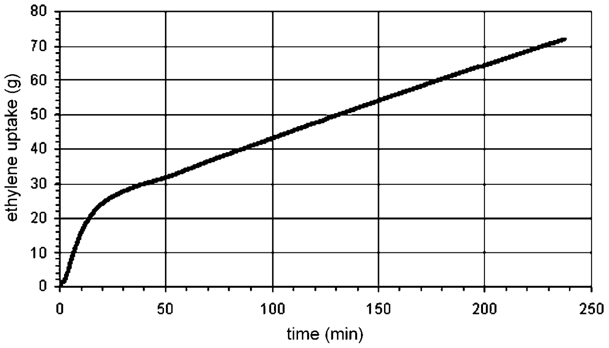


Figure 1. Ethylene-uptake curve for a typical ethylene trimerization reaction catalyzed by the $[CrCl_3(thf)_3]$/PNPNH/$AlEt_3$ catalyst system. (Run conducted at 65 °C, 30 bar, $[Cr]=1\ mmol\,L^{-1}$, $t=4$ h, $[L]/[Cr]=1.5$ mol/mol, $[Al]/[Cr]=70$ mol/mol.)

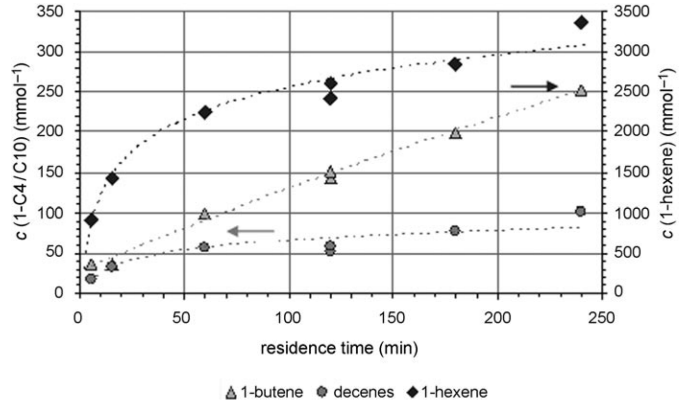


Figure 2. Concentration–time profile of the formation of 1-hexene and the most important by-products 1-butene and branched decenes with the $[CrCl_3(thf)_3]$/PNPNH/$AlEt_3$ catalyst system. (Runs conducted at 65 °C, 30 bar, $[Cr]=1\ mmol\,L^{-1}$, $[L]/[Cr]=1.5$ mol/mol, $[Al]/[Cr]=70$ mol/mol.)

Nevertheless, besides 1-hexene, also 1-butene and branched decenes are formed as major by-products. Whereas the trimerization of ethylene follows the kink kinetics, the rate of the dimerization towards 1-butene is nearly constant right from the beginning of the reaction. After approximately one hour, the ratio of the formation rates of 1-hexene and 1-butene decreases slightly, leading finally to a decline in the C6 selectivity over time. The formation of 1-butene might be the result of an early β-H elimination of the C4 chain from the chromacyclopentane.[24] However, due to the different kinetics of the formation of 1-butene in contrast to 1-hexene, it is doubtful whether the same catalytically active species is responsible for both 1-olefins and whether 1-butene is actually an inherent side product of the catalytic cycle for 1-hexene. Accordingly, a different mechanism from the metallacycle route, for example, insertion/β-H elimination, is conceivable as well and was in fact proposed for the nickel-catalyzed ethylene dimerization.[25] Unfortunately, only very little is known about the mechanism of the formation of 1-butene as a typical by-product during ethylene trimerization because the gas-phase product was not analyzed in most of the cases.

In contrast, the concentration of branched decenes increases in parallel with the concentration of 1-hexene, which results in a constant mass relation of the C10 fraction to 1-hexene over time (about 3 wt% of total product). Branched decenes seem to be an inherent by-product of selective ethylene oligomerization and were observed in several catalytic systems.[7e,8,14,17] They are the result of secondary incorporation reactions, in which the primary product 1-hexene competes with ethylene either in the coupling reaction resulting in butyl-substituted chromacyclopentanes or in the subsequent insertion into the chromacyclopentane. Unfortunately, it was not possible to conclude which pathway is applicable, since the identification of the different C10 isomers was not successful due to poor differentiation with GC–MS. Whereas Hagen[8] found indications that the insertion of 1-hexene in the metallacyclopentane is more likely, Deckers et al.[26] postulated that 1-hexene is incorporated during the coupling reaction. Regardless of what actual route the reaction takes in detail, the effective reaction rate of cotrimerization with 1-hexene is presumably much slower than the rate of ethylene trimerization itself. This observation has significant consequences with respect to the overall kinetics. Depending on the actual ethylene/1-hexene ratio, a significant part of the active catalytic species will be 'blocked' by the slower cotrimerization reaction. If this is true, one would also predict an increasing reversible inhibition of the catalyst as more and more product is being formed,[8] which results in decreasing activity with increasing 1-hexene concentration.

Effect of ethylene pressure: To elucidate the influence of ethylene concentration on the performance of the novel chromium-catalyzed ethylene trimerization system, the ethylene pressure was varied at 65 °C in the range of 10 to 60 bar with 10 bar increments.

From the ethylene-uptake curve of 10, 30, and 50 bar in Figure 3, several effects can be observed. The first observation is that the rate of ethylene uptake increases with increasing ethylene concentration, while the time characteristics still show the typical kink kinetics. This leads to the conclusion that the ethylene concentration is not the determining factor for the strong loss in activity after an initial phase of about 20 min (at 50 bar). Secondly, the induction period, which indicates the time required for the formation of the active catalytic species (time period between ethylene pressurization and start of trimerization reaction), follows the same pattern of about 2.5 min for each pressure. Consequently, one can conclude that the catalyst's activation is not strongly affected by ethylene concentration.

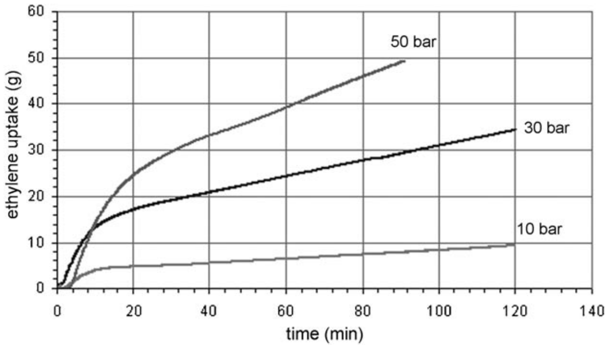


Figure 3. Effect of pressure on the total ethylene uptake of the [$CrCl_3(thf)_3$]/PNPNH/$AlEt_3$ catalyst system. (Runs conducted at 65 °C, [Cr] = 1 mmolL^{-1}, [L]/[Cr] = 1.5 mol/mol, [Al]/[Cr] = 70 mol/mol.)

Considering the initial activity, where interference with secondary effects is not yet very likely, as a function of ethylene pressure (Figure 4), the direct proportionality of the initial activity with respect to ethylene pressure becomes evident in the measured pressure regime from 10 to 60 bar. On the basis of Henry's law and the fact that the phase transfer of ethylene to toluene is fast relative to the reaction, one can deduce a first-order dependency of the initial activity (a_i) with respect to the ethylene concentration ($c^*_{Et,L}$ in the liquid phase) [Eq. (1)]:

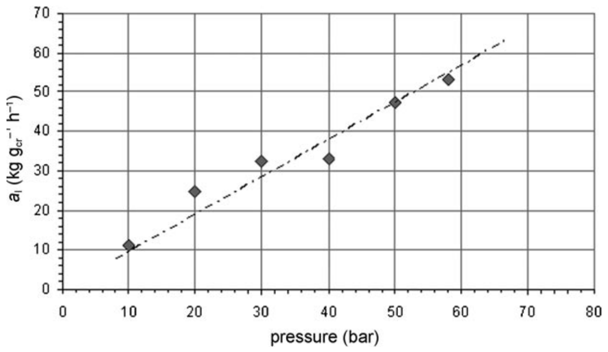


Figure 4. Effect of pressure on the initial activity of the [$CrCl_3(thf)_3$]/PNPNH/$AlEt_3$ catalyst system. (Runs conducted at 65 °C, [Cr] = 1 mmolL^{-1}, [L]/[Cr] = 1.5 mol/mol, [Al]/[Cr] = 70 mol/mol.)

$$a_i \sim (c^*_{Et,L})^1 \qquad (1)$$

Of course, this "first approximation" of the reaction order by means of the pressure dependency of the initial activity gives only an "integrated" order over the entire catalytic process, inherently including all side reactions, like 1-butene or branched-decenes formation. However, because of the high selectivity towards 1-hexene, this observed first-order dependency of the ethylene trimerization with respect to ethylene concentration appears rather conclusive.

As discussed previously, some discrepancies do exist regarding the influence of ethylene concentration on the selective oligomerization processes. In contrast to the experimental observations of this study, Manyik et al.,[5] Yang et al.,[17] and Wass et al.[13e] reported a second-order dependency for different chromium-based catalyst systems. A first-order dependency, as observed here, is supported by several theoretical modeling studies,[18–20] and was also observed experimentally by Kuhlmann[15] for the trimerization reaction using Sasol's "Cr–PNP" tri- and tetramerization catalyst system.

Investigation of temperature dependency: The next set of experiments consists of a temperature variation from 30 to 90 °C at otherwise constant parameters in which isothermal conditions were ensured during all experiments. The selectivity decreases dramatically above 60 °C (up to 84 wt % at 90 °C) due to the increased formation of the main by-product 1-butene at elevated temperatures.

The ethylene-uptake curves at selected temperatures are compared in Figure 5. It becomes evident that increased temperature affects the kinetic behavior of the trimerization catalyst system in different ways. Firstly, the curvature of the ethylene uptake changes completely from smoothly shaped with nearly constant consumption over time at low temperatures, to the already discussed kink kinetics at temperatures above 60 °C. The strong kink is presumably the result of the catalyst's deactivation or a change in the nature of the catalyst's active species at high temperatures, leading to a less active catalytic species. Naturally, this process is also driven by temperature-dependent kinetics with its own activation energy. Hints on a molecular level were already given by the mechanistic investigation of the influence of elevated temperatures on the PNPNH/AlEt$_3$ system.[23] It could be proven that, at higher temperatures, a ligand rearrangement takes place in the presence of AlEt$_3$. Although this effect was not verified until now for the chromium-containing catalyst system, an analogous process might be a possible explanation for the catalyst deactivation and the observed kink in the ethylene-uptake curve.

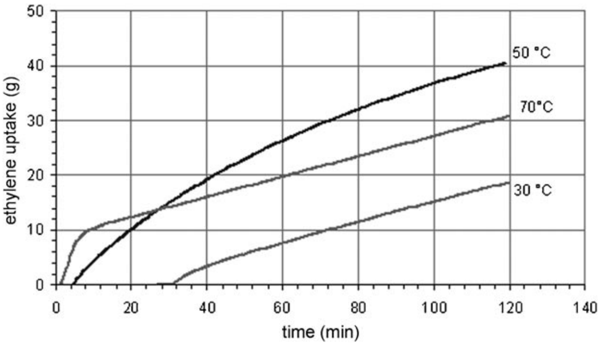


Figure 5. Effect of temperature on the total ethylene uptake of the [CrCl$_3$(thf)$_3$]/PNPNH/AlEt$_3$ catalyst system. (Runs conducted at 30 bar, [Cr] = 1 mmol L^{-1}, [L]/[Cr] = 1.5 mol/mol, [Al]/[Cr] = 70 mol/mol.)

The catalyst activation is also strongly affected by temperature. For example, at 30 °C, the trimerization reaction did not start until 30 min after pressurization with ethylene, whereas the induction period at 65 °C lies around 2.5 min. This leads to the aforementioned conclusion that the catalytically active species has still to be formed in the presence of ethylene. During activation with AlEt$_3$, the deprotonation of the ligand, the consecutive coordination to the chromium, and a further interaction of the catalytically active species with ethylene is most likely. Naturally, all these individual reaction steps are determined by their own temperature-dependent kinetics.

From Figure 5, it is clear that the maximum rates observed in the beginning of each run and reflecting the intrinsic reaction rate of the catalytic trimerization reaction prior to catalyst deactivation processes, increase strongly with increasing temperature. By interpreting the temperature dependency of the reaction rate/activity, one has, of course, to take into account that the equilibrium concentration of ethylene $c^*_{\mathrm{Et,L}}$ in the liquid phase is also a strong function of temperature (T) [Eq. (2) in which p_{Et} is the ethylene pressure and H_{Et} is the Henry constant for ethylene in toluene].[27]

$$c^*_{\mathrm{Et,L}} = p_{\mathrm{Et}}H_{\mathrm{Et}} = p_{\mathrm{Et}}e^{\left(\frac{1228k}{T} \ -6.12\right)} \tag{2}$$

The obtained direct proportionality between the initial activity and the ethylene concentration helps to describe the temperature dependency of the initial activity. Therefore, a simplified approach to describe the relation between initial activity and both temperature and ethylene concentration was applied [Eq. (3), in which k_{i} [s^{-1}] represents the temperature-dependent reaction rate constant for the trimerization reaction (4) and k_{i0} is a pre-exponential factor].

$$a_{\mathrm{i}} \sim k_{\mathrm{i}}(c^*_{\mathrm{Et,L}})^1 \tag{3}$$

$$k_{\mathrm{i}} = k_{\mathrm{i0}}e^{-\frac{E_{\mathrm{a}}}{RT}} \tag{4}$$

Figure 6 shows the Arrhenius diagram of the reaction rate constant k_{i} derived from the quotient of the initial activity a_{i} and the theoretical ethylene equilibrium concentration $c^*_{\mathrm{Et,L}}$. In the range from 30 to 70 °C, the reaction rate follows the typical Arrhenius behavior with an experimentally derived apparent activation energy (E_{a}) of 52.6 kJ mol^{-1}. At 70 °C, a relatively abrupt change of this empirical apparent activation energy is observed, giving approximately 12.7 kJ mol^{-1}

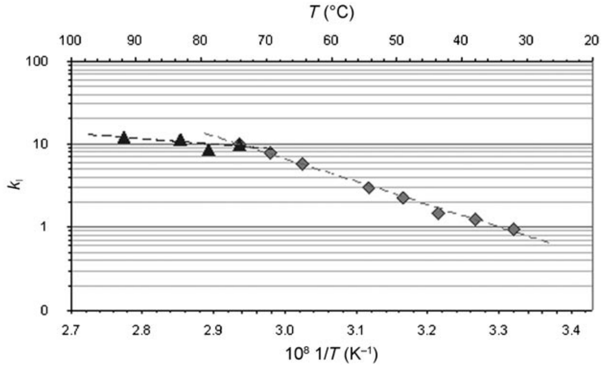


Figure 6. Effect of temperature on the initial rate constant k_{i} of the [CrCl$_3$(thf)$_3$]/PNPNH/AlEt$_3$ catalyst system. (Runs conducted at 30 bar, [Cr] = 1 mmol L^{-1}, [L]/[Cr] = 1.5 mol/mol, [Al]/[Cr] = 70 mol/mol.)

for temperatures between 70 and 90 °C. The reason for this behavior could be a very rapid onset of the catalyst deactivation. It is also conceivable that elevated temperatures might prevent the catalyst's complete activation with the consequence that not the entire, theoretically possible, amount of catalyst is involved in the trimerization reaction. The pronounced reduction in the activation energy may also be explainable by the strongly incipient 1-butene formation at elevated temperatures. However, this general interpretation is slightly simplified, since the trimerization relies on a complex reaction network.

After all, one has always to consider that the empirical kinetic figures are based on the interpretation of the initial slope of the ethylene-uptake curves, reflecting the reaction in its entirety, which means that all side reactions are included. Due to the long activation period, depending on the temperature, it is quite possible that the derived initial activity might slightly interfere with the formation of the active catalytic species.

As mentioned earlier, only few publications[8a,14,15] deal with kinetic investigations of selective ethylene oligomerization catalyst systems. Currently, only one extensive report on kinetic measurements is known for an ethylene tri- and tetramerization system; it consists of the precatalyst [Cr(acac)$_3$], Ph$_2$PN(*i*Pr)PPh$_2$ as ligand, and MAO as activator.[14] It is very interesting that the published results, with respect to temperature effects, are in several points in good agreement with the ones discussed here, although Sasol's "Cr–PNP" system is able to tetramerize ethylene as well. Walsh et al. found a comparable temperature effect on the ethylene-uptake behavior by regarding the increase in curvature of the uptake curve profile with increasing temperature, which also resulted in a kind of kink kinetics at 60 °C. The catalyst's activation is a function of temperature as well. It was found that the initial reaction rate follows a typical Arrhenius behavior with an apparent activation energy of 64.6 kJ mol^{-1} in the temperature range between 35 and 45 °C, lying in the same regime as for the "Cr–PNPNH" system. In contrast to the system of this investigation, the "Cr–PNP" system starts to deactivate at even lower temperatures of around 45 °C.[14,15]

Influence of catalyst concentration: To investigate the influence of the catalyst concentration on the catalytic performance of the "Cr–PNPNH" system, the concentration was varied in the range of 0.25 and 1.5 mmol L^{-1} at constant ligand/chromium and Al/chromium molar ratio.

The averaged apparent activity for all concentrations is in the range of 5.0 kg(g$_{Cr}$ h)$^{-1}$. This indicates a first-order dependency in catalyst concentration, which is confirmed by Figure 7, which shows the ethylene-uptake curves of experiments with 50 % more and 50 % less catalyst concentration than in the standard case.

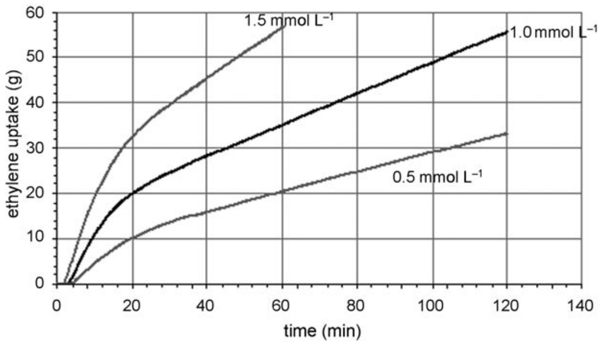


Figure 7. Effect of catalyst concentration on the total ethylene uptake of the [CrCl$_3$(thf)$_3$]/PNPNH/AlEt$_3$ catalyst system. (Runs conducted at 65 °C, 30 bar, [L]/[Cr] = 1.5 mol/mol, [Al]/[Cr] = 70 mol/mol.)

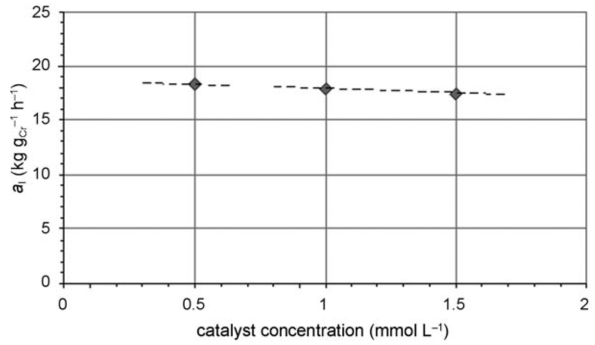


Figure 8. Effect of catalyst concentration on the initial activity of the [CrCl$_3$(thf)$_3$]/PNPNH/AlEt$_3$ catalyst system. (Runs conducted at 65 °C, 30 bar, [L]/[Cr] = 1.5 mol/mol, [Al]/[Cr] = 70 mol/mol.)

When the initial activity is derived from the ethylene-uptake curve (Figure 8) and normalized with the catalyst amount, the first-order dependency in the catalyst concentration is undeniable. Later on, secondary effects influencing the reaction kinetics, like the big difference in liquid-phase composition and amount, presumably leads to the observed discrepancy. The results also confirm that the experiments are not inadvertently compromised by gas-to-liquid mass-transfer limitations.

In general, the observed first-order dependency was expected and is in good accordance with the findings of Hagen for the Ti-based trimerization system[8a] and with the results of Walsh et al. for the Cr-based tri- and tetramerization system.[14]

Effect of ligand/chromium ratio: Besides process conditions like residence time, temperature, or ethylene pressure, the catalyst composition has a major influence on the catalytic performance as well. This pertains in particular to the molar ratio of ligand to chromium and to the molar ratio of cocatalyst to chromium. In the first step, the molar ratio of the PNPNH ligand to the chromium precursor [CrCl$_3$(thf)$_3$] was varied in the range from 0.5 to 3.0.

From Figure 9 it becomes clear that the average activity is a strong function of the molar ligand/chromium ratio, with a distinctive maximum at [L]/[Cr] = 1.75, which indicates that at this ratio, the highest number of catalytically active species for ethylene trimerization is formed. The corresponding overall 1-C6 selectivity shows a similar dependency on the

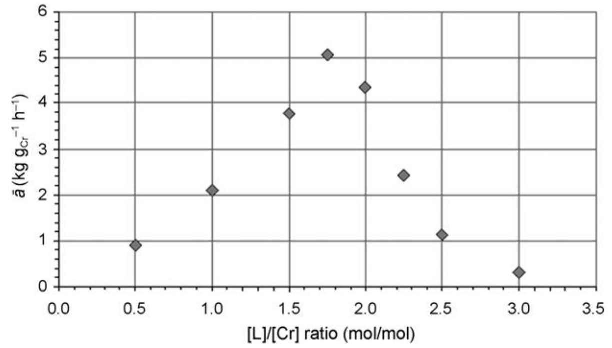


Figure 9. Effect of molar ligand to chromium ratio on the average activity of the $[CrCl_3(thf)_3]$/PNPNH/$AlEt_3$ catalyst system. (Runs conducted at 65 °C, 30 bar, 120 min, $[Cr]=1.0\ mmol\,L^{-1}$, $[Al]/[Cr]=70$ mol/mol.)

ligand/Cr molar ratio, which also has a maximum between 1.5 and 1.75 (Figure 10), whereas the value at a ratio of 3.0 is an experimental uncertainty. The decrease in selectivity at low and high ratios can be traced back to an increased formation of 1-butene, while the decene fraction remains constant for the entire experimental series.

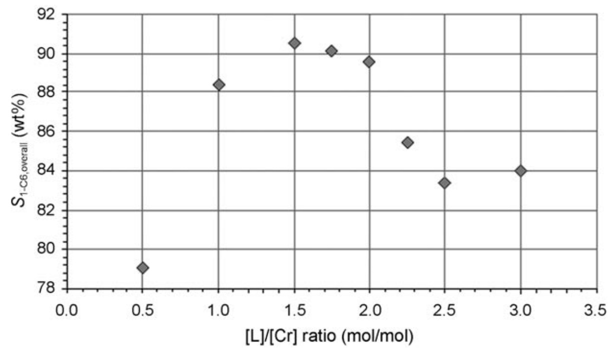
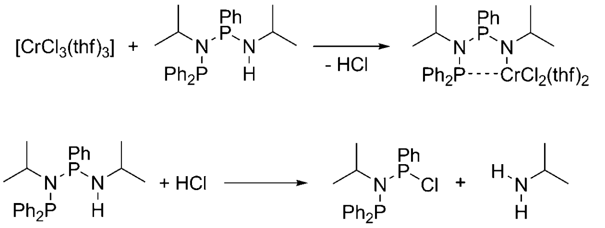


Figure 10. Influence of the molar ligand to chromium ratio on the 1-C6 selectivity overall of the $[CrCl_3(thf)_3]$/PNPNH/$AlEt_3$ catalyst system. (Runs conducted at 65 °C, 30 bar, 120 min, $[Cr]=1.0\ mmol\,L^{-1}$, $[Al]/[Cr]=70$ mol/mol.)

At first glance, the observation that both activity and selectivity show a maximum at a noninteger ligand/chromium molar ratio seems very surprising. There is little doubt that the active trimerization catalyst consists of one mononuclear chromium center with one attached PNPNH ligand.[23] In general, one can conclude that the formation of the catalytically active site is the result of a complex reaction equilibrium involving all three catalyst components, which leads to the requirement of a large excess amount of ligand to reach an optimum in activity.

One reason for the need of a large excess amount of ligand relative to chromium might be that part of the ligand decomposes during the activation procedure. During the coordination of the PNPNH ligand to $[CrCl_3(thf)_3]$ the NH function of the ligand is deprotonated under potential liberation of HCl. In a further step, the free HCl is able to split a noncoordinated ligand molecule into several phosphorous- or nitrogen-containing fragments (Scheme 2). ^{31}P NMR spectroscopy studies, stability investigations of the $[CrCl_3(thf)_3]$/ligand slurry, and the isolation and characterization of an ammonium-ate complex of the PNPNH ligand coordinated to chromium tetrachloride, as a result of the ligand fragments interacting with the chromium center, gave indication that this decomposition occurs. Consequently, the ligand also acts as scavenger for the liberated HCl during catalyst activation.



Scheme 2. Possible reaction mechanism for the observed PNPNH ligand decomposition.

However, on the other hand, a big surplus of ligand also reduces the catalytic performance with regard to activity and selectivity. Clearly, more than one ligand can coordinate to chromium and hence shield the free coordination site, which is necessary for the coordination of two ethylene molecules. Summing up, it becomes evident that a very fine balance between the amount of PNPNH ligand and chromium precursor needs to be maintained, which is very susceptible to small variations.

Effect of $AlEt_3$/chromium ratio: As shown in several studies,[13e,17,28] the catalytic performance of selective oligomerization catalyst systems is also a function of the ratio of cocatalyst to catalyst. Therefore, the molar ratio of triethylaluminum to chromium, in the following abbreviated as Al/Cr ratio, was varied over a wide range between 5 and 170 at otherwise constant process conditions for the “Cr–PNPNH” trimerization catalyst system.

The Al/Cr ratio has a certain effect on the selectivity; thus C6 selectivity and 1-hexene purity increase drastically with decreasing Al/Cr ratio below 25, whereas at higher ratios the influence is not as significant.

For the interpretation of the time characteristics of the trimerization reaction as a function of the Al/Cr ratio, selected ethylene-uptake curves are shown in Figure 11. At ratios above 70 the typical kink kinetics is observed, whereas with an increasing excess of $AlEt_3$ the kink in the ethylene-uptake curve becomes sharper and occurs earlier. Interestingly, both the initial and the final ethylene consumption rate for molar ratios of 70 and 170 seem to be in the same regime, leading to the conclusion that the amount of aluminum alkyl finally has no influence on the number of deactivated catalyst species after the kink. With decreasing Al/Cr ratio, the curvature of the ethylene-uptake curves decreases

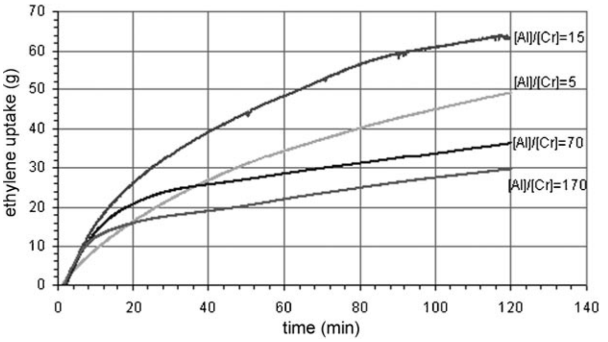


Figure 11. Effect of the $AlEt_3$/Cr ratio on the total ethylene uptake of the $[CrCl_3(thf)_3]$/PNPNH/$AlEt_3$ catalyst system. (Runs conducted at 65 °C, 30 bar, $[Cr] = 1\ mmol\,L^{-1}$, $[L]/[Cr] = 1.5$ mol/mol).

as well, eventually leading to a smoothly bent ethylene-uptake curve for a Al/Cr molar ratio of 15. However, the initial slopes of all ethylene-uptake curves of experiments with Al/Cr molar ratios above 15 are identical, while at ratios below 15 a decline is observed, which indicates that not the entire number of possible catalytic species is activated. The induction period for all Al/Cr molar ratios is 2.5 min, a typical value for experiments conducted at 65 °C. Consequently, the kinetics of catalyst activation do not seem to be a function of the amount of $AlEt_3$ relative to chromium.

In general, it becomes clear that no large excess of the aluminum alkyl is necessary to activate the catalyst and, moreover, that such an excess even has detrimental effects on the catalytic performance, as was already shown for the "Cr–PNP/SNS" trimerization system.[13c,28b] The optimum lies around 15 mol cocatalyst per 1 mol chromium, which is presumably also dependent on the amount of impurities scavenged by the aluminum alkyl. This is quite low in comparison with the "Cr–PNP" tri- and tetramerization catalyst system, for which at least 190 equiv MAO per 1 equiv chromium are required for a complete activation, while a surplus of MAO does not seem to have any impact on the catalytic performance.[14]

Due to the fact that, besides the chromium precursor, the PNPNH ligand also interacts intensely with the cocatalyst, the essentially required amount of $AlEt_3$ for catalyst activation is also a function of the molar ratio of PNPNH ligand to chromium. Thus, a deprotonation of the ligand's amine function occurs presumably during activation, while a coordination of the PNPNH ligand to the aluminum atom is also possible.[23] Both, ligand deprotonation[13c,d,28b,29] and further interaction with/stabilization of the active site by a chelating framework[28b,30] is conceivable and was verified for several systems.

Assuming that the ligand rearrangement at elevated temperatures, as discussed in ref. [23], is responsible for the deactivation, eventually leading to the observed kink in the ethylene-uptake curve, one can conclude that this process of deactivation is also a function of the excess amount of aluminum alkyl. For low Al/Cr molar ratios (e.g., 15) the kink is not as distinctive, supposedly for the reason that not enough 'free' $AlEt_3$ can compete with chromium for the PNPNH ligand and initiate a rearrangement of the ligand leading to a less active catalyst species. At higher Al/Cr molar ratios, the equilibrium is shifted towards $AlEt_3$, making a deactivation more likely, which again becomes evident in the ethylene-uptake curve. However, even through the simple interaction of the ligand with $AlEt_3$, like the formation of Al–amide bonds, the number of available ligand molecules for the chromium-based trimerization catalyst is reduced.

Conclusion

The reported experimental series were carried out to investigate the influence of single parameters on the novel "Cr–PNPNH" trimerization catalyst system, while all other process parameters were held constant. The results are required for a better understanding of the catalytic system and they deliver data for an upscaling of the process. The catalyst system was not only defined by its chemical composition and structure, but also by its individual window of operability in terms of process conditions and catalyst composition. The high number of possible process parameters comprises a multidimensional parameter (hyper)space, in which the catalyst can act. Consequently, the establishment of the best set of parameters to reach an optimum in catalytic performance is a great challenge.

However, some basic concepts for the novel trimerization catalyst can be derived from previous results.

First of all, in the beginning the applied catalyst consists of its single components. These are the chromium precursor $[CrCl_3(thf)_3]$ and the PNPNH ligand, which finally form the active catalytic species in situ, by activation with $AlEt_3$ in the presence of ethylene. It is most likely that the PNPNH ligand is just a precursor and undergoes deprotonation upon addition of $AlEt_3$, a reaction that is also highly dependent on the reaction temperature.

It could be shown that the ethylene concentration has a significant influence on the catalytic performance. So the initial activity shows a first-order dependency on the ethylene concentration. Also, a first-order dependency was found for the catalyst concentration. The initial activity follows a typical Arrhenius behavior with an experimentally determined activation energy of $52.6\ kJ\,mol^{-1}$. Therefore, a simplified expression for the initial activity could be derived [Eq. (5)]:

$$a_i \sim e^{-\frac{52.6\ \mathrm{kJ\,mol^{-1}}}{RT}}(c^*_{\mathrm{Et,L}})^1(c_{\mathrm{catalyst}})^1 \tag{5}$$

This empirically derived expression describes the dependency of the initial activity of one single catalytic system, defined by its specific chemical composition ($[L]/[Cr] = 1.5$ mol/mol, $[Al]/[Cr] = 70$ mol/mol) only. However, it could be also shown that the molar composition of the individual catalytic components has a significant effect as well. This means that the pressure and temperature dependencies might vary with different catalyst compositions.

At elevated temperatures (ca. 80 °C) a significant deactivation was observed, which can be tentatively traced back to a ligand rearrangement in the presence of $AlEt_3$. After a fast initial phase, a pronounced kink in the ethylene-uptake curve was observed, followed by a slow, almost linear, further increase of the total ethylene consumption. Although it is not clear so far whether the ligand rearrangement is really responsible for the deactivation, one can still assume that, at high temperatures, the catalytically active species is converted to a less active one. Moreover, some evidence for competitive reversible product inhibition was found, which also had a significant effect on the kinetics. The formation of branched decenes is an indication of this blocking of the active sites by the product, since this side reaction reflects the "irreversible part" of this blocking process.

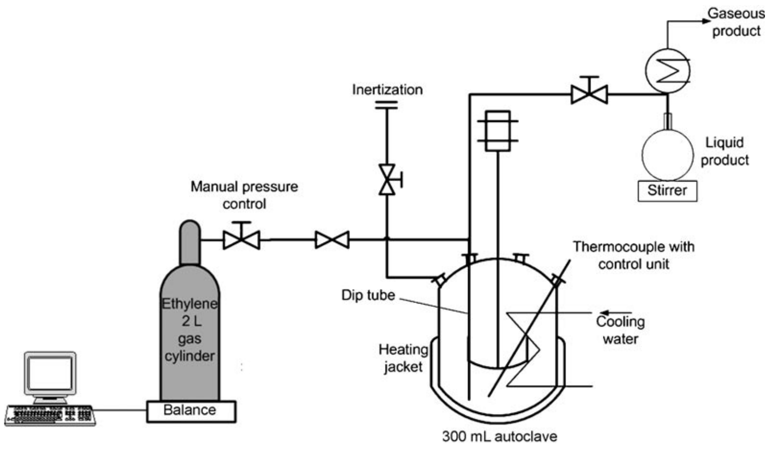


Figure 12. Schematic of the 0.3 L Parr kinetic test rig.

However, all concepts developed so far for a reaction mechanism are based on one single catalyst system chosen from a large family of catalysts consisting of a chromium precursor and a ligand with the basic chemical structure PNPNH. Through variation of substituents of the ligand, through the variation of the chromium precursor, or even through the choice of the solvent, the kinetics can be influenced fundamentally.

Experimental Section

Materials: For the selective oligomerization experiments, the following chemicals were used: $[CrCl_3(thf)_3]$ (97 % purity) and $AlEt_3$ solution (1.9 mol L^{-1} in toluene) was obtained from Sigma–Aldrich and used without further purification; toluene (>99.9 % purity) was obtained from Merck Chemicals and was dried over sodium with benzophenone and was then distilled in an inert gas atmosphere (Ar); argon 5.0 and ethylene 3.0 were purchased from Linde Gas and used as received; the $Ph_2PN(i\mathrm{Pr})P(Ph)N(i\mathrm{Pr})H$ (PNPNH) ligand was synthesized according to published procedures.[22,23] All air- and moisture- sensitive compounds were handled under an argon atmosphere using standard Schlenk techniques or in a glove box.

Experimental setup and procedural methods for ethylene trimerization: The syntheses were performed in a 0.3 L Parr autoclave equipped with a hollow-shaft gas-entrainment stirrer. The ethylene supply was maintained by an aluminum pressurized gas cylinder on a balance to monitor the ethylene consumption over time by means of a computerized data-acquisition system. The ethylene-supply pressure was controlled by a pressure reducer, which held the pressure constant over the entire run time. The temperature of the autoclave was measured by a thermocouple inside the reactor's liquid phase and controlled electronically by an electrical heating jacket and a water cooling coil, submerged in the liquid phase. The autoclave could be depressurized and evacuated by means of a rotary vane vacuum pump (10^{-1} mbar). A low-pressure argon supply (1.5 bar absolute) was used to obtain an inert atmosphere. A schematic of the experimental test rig is given in Figure 12. Before conducting an experiment, the reactor was heated to 100 °C at reduced pressure for several hours and purged with argon several times to eliminate traces of water and oxygen. The reactor was then allowed to cool down to reaction temperature and the prepared catalyst solution was transferred to the evacuated reactor by means of the pressure differential to the argon inert atmosphere. The speed of the gas entrainment stirrer was set to 1000 rpm to exclude gas-to-liquid mass-transfer limitations. In the next step, the reactor was pressurized with ethylene to start the experiment. All reactions were performed at a constant reaction temperature. After the reaction time the ethylene supply was closed and the reaction solution was discharged by transferring the liquid by means of the headspace pressure via the reactor's dip tube into a round-bottomed flask with HCl-acidified water for rapid catalyst quenching. The volume of the gaseous product phase was measured by a gas meter and collected completely in a gas bag. The mass balance of the experiment was determined by quantification and GC/flame ionization detection (FID) analysis of the gaseous and liquid product separately, followed by comparison with the ethylene-uptake data.

Catalyst preparation: The catalyst was always activated ex situ under argon. Hence, the required amount of the chromium precursor ($[CrCl_3(thf)_3]$) and the PNPNH ligand were weighed under an inert atmosphere. Then the catalyst components were transferred into a Schlenk tube and dissolved under stirring in anhydrous toluene (100 mL). After suspending the Cr compound and the ligand, the required amount of $AlEt_3$ was added, yielding the activated catalyst solution. The solution was immediately transferred to the suitably tempered reactor and the reaction was started by opening the ethylene supply.

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